Prof Remsen

The Double Halides of Antimony

—WITH—

Aniline and the Toluidines

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

—BY—

HOWARD H. HIGBEE

1895

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TABLE OF CONTENTS:

Acknowledgment 4
Introduction 5
Methods of Analysis 9
Description of Experiments 10
Experiments with Aniline Hydrochloride and Antimony Trichloride 11
Experiments with *o*-Toluidine Hydrochloride and Antimony Trichloride 15
Experiments with *m*-Toluidine Hydrochloride and Antimony Trichloride 17
Experiments with *p*-Toluidine Hydrochloride and Antimony Trichloride 19
Experiments with Aniline Hydrobromide and Antimony Tribromide 21
Experiments with *o*-Toluidine Hydrobromide and Antimony Tribromide 24
Experiments with *m*-Toluidine Hydrobromide and Antimony Tribromide 26
Experiments with *p*-Toluidine Hydrobromide and Antimony Tribromide 28
Experiments with Aniline Hydriodide and Antimony Triiodide 30
Experiments with *o*-Toluidine Hydriodide and Antimony Triiodide 33
Experiments with *m*-Toluidine Hydriodide and Antimony Triiodide 35
Experiments with *p*-Toluidine Hydriodide and Antimony Triiodide 37
List of Compounds described 39
Conclusion 39
Biographical 40

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INTRODUCTION.

There have been known for a long time a large number of substances which it has been impossible to harmonize with regular chemical compounds according to the recognized views of valence.

These substances have received various descriptive terms, which were intended to explain their character, but as long as the nature of the substances was not well understood, of course, any number of names would not accomplish the desired end.

As examples of these terms may be mentioned those of molecular compounds, addition products and double salts.

On account of the obscure nature of these substances they are generally ignored, or given a merely passing notice in the text-books.

A few years ago Professor Remsen reviewed the literature of the subject and presented in a concise article[1] all that is known regarding the matter and has supplemented this knowledge by the statement of a law which seems to underlie the formation of all double halides.

Before stating this law and discussing the facts which led to its detection, it may not be out of place in this connection to give a brief resumé of some of the views that have been held upon the subject of the double halides.

In general, a double halide compound consists of the chemical union of the halide of a basic element or group of elements having basic properties, with the corresponding halide of some more acidic element; for example, potassium chloride with antimony trichloride, to form potassium chlorantimonite, $KCl.SbCl_3$; or again, aniline hydrochloride unites with antimony trichloride to form aniline chlorantimonite, $C_6H_5NH_2.HCl.SbCl_3$, etc.

It is a rather remarkable fact that the number of double halides which consist only of univalent elements is very small.

Many of the bivalent elements, such as those arranged in

[1] Am. Chem. J., 11, 291.

Group II of the Periodic System, form two series of double halides with univalent metals of the first group ; for example, $MgCl_2.KCl$ and $MgCl_2.2KCl$.

The halogen salts of the trivalent elements, such as bismuth, antimony and chromium, form in a similar way three classes of compounds.

Leaving out of account all double ammonium salts whose formation seems to depend upon some law peculiar to nitrogen, it has been observed that almost without exception there is a certain definite regularity to which all other double halides conform.

Stated in the words of Prof. Remsen, the law is as follows:

"*When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms contained in the latter.*"

At the time the article referred to was written it was stated that out of over four hundred double halides there was but one which did not seem to conform to the above law. This compound has the composition $CuCl(KCl)_2$. By an extension of the theory which was framed to explain the constitution of other double halides, this compound has been satisfactorily accounted for. The discussion of this will be taken up a little later.

On examination of certain oxygen compounds formed by the substitution of metallic hydroxides in the hydroxides of the alkali metals, a striking analogy to the double halides is seen, both as respects the mode of formation and the composition.

As examples of the above mentioned oxygen compounds, the following may be cited :

$$Zn\begin{matrix}-OH\\-ONa\end{matrix} \quad Pb\begin{matrix}-OK\\-OK\end{matrix} \quad Al\begin{matrix}-ONa\\-ONa\\-ONa\end{matrix} \quad Al\begin{matrix}=O\\-ONa\end{matrix}$$

Compared with the alkaline hydroxides, the other hydroxides are acidic ; so in the double halides there is a union between a relatively acidic halide salt with a relatively basic

halide salt. Furthermore, the analogy in the composition of these oxygen compounds with the double halides is seen by an inspection of formulas of both classes of compounds; for example, $NaAlO_2$ and $NaAlCl_4$, in which two oxygen atoms are equivalent to four chlorine atoms or rather play an analogous rôle.

v. Bonsdorff[1] and Boullay,[2] independently of each other, were the first to point out the distinction between acidic and basic halides. This view was objected to by Liebig[3] and later by Berzelius,[4] on the ground that if a substance was a salt it could possess neither acidic nor basic properties.

This objection has had great influence in the non-acceptance by chemists of the view of v. Bonsdorff and Boullay, and little was heard of their theory until about the year 1840, when Dr. Hare, of Philadelphia, offered the following definition of salts:

"*When two compounds capable of combining with each other to form a tertium quid, have an ingredient common to both, and one of the compounds prefers the positive and the other the negative pole of the voltaic series, we must deem the former an acid, the latter a base.*"

Granting the analogy in composition and mode of formation to exist between the oxygen salts and the double halides, the structure of the latter finds easy explanation.

Naquet[5] expressed himself on this point in 1867 in his Principles of Chemistry, by suggesting that *two halogen atoms acting together can play the same part that the so-called linking oxygen atom plays in oxygen salts.* He gives the formula Ag—Cl—Cl—K to illustrate his idea.

Views of a similar nature have been advanced by Bloomstrand[6] in 1869, by Jörgensen[7] in 1877, by Mallet[8] in 1881, and by others. Certain objections to the theory that two

1 Ann. chim. phys., **34**, 142.
2 *Ibid.*, **34**, 337.
3 *Ibid.*, **35**, 68.
4 Jahresb., **8**, 138.
5 Principes de Chimie fondeé sur les Théories modernes, p. 62, par H. Naquet, Paris, 1864.
6 Chem. d. Jetztzeit, p. 340.
7 J. prakt. Chem., **16**, 352.
8 Am. Chem. J., **3**, 189.

halogen atoms may play the rôle of the linking oxygen atom have been urged.

Among the foremost of these is that of Horstmann, which appeared in his Theoretische Chemie, p. 340. It is simply that the view is not in accordance with the prevailing ideas regarding the valence of the halogens. In the present condition of the knowledge respecting valence, this objection is not a very forcible one.

More recently other objections have been brought forward, but they will not be taken up in this place.

Recent researches in the field of double halides have brought to light the existence of certain compounds of this order which do not find satisfactory explanation by means of the views thus far held, making it necessary, therefore, to somewhat extend the theory. There are, for example, the two salts, $CuCl.2KCl$ and $CdCl_2.4KCl$. The former salt, discovered by Mitscherlich,[1] has been re-investigated and found to exist.

The second salt, found by v. Hauer,[2] has also been re-examined, and, it is believed, has the formula assigned to it.

There have since been found other compounds of this character which cannot be explained by the hypothesis of the double halogen atom acting as a bivalent group. Three such compounds have been brought to light in the course of the present investigation.

The compounds referred to are *tetraniline bromantimonite*, $(C_6H_5NH_2HBr)_4.SbBr_3.H_2O$, and *tetra-p-toluidinebromantimonite*, $(C_6H_4.CH_3.NH_2.HBr)_4.SbBr_3$, and *tetraniline iodantimonite*, $(C_6H_5.NH_2.HI)_4.SbI_3$.

In all such exceptional cases Prof. Remsen[3] suggests that it seems necessary to assume that three halogen atoms acting together form a trivalent group $>(Cl)_3$— or, assuming that chlorine is trivalent, the group must be represented structurally thus: $—Cl\begin{matrix}/Cl— \\ | \\ \backslash Cl—\end{matrix}$.

The above is a brief account of the subject of double halides.

[1] Ann. chim. phys., **73**, 384.
[2] J. prakt. chem., **64**, 486.
[3] Am. Chem. J., **14**, 87.

Following is a description of an investigation of the action of three of the halides of antimony, the chloride, bromide and iodide upon aniline, ortho-, meta-, and para-toluidine, with a view to determining what compounds can be formed from these substances and what was of more importance, the law governing their formation.

Methods of Analysis.

Antimony and the halogen only were determined in each salt.

Determination of Antimony.

About 0.3 gram of the dried salt was weighed off, and after dissolving in a few cc. strong solution of tartaric acid, the whole was considerably diluted with water and heated to boiling.

The solution was then acidified with sulphuric acid and a current of washed hydrogen sulphide passed into the solution for some time. When the antimony had been completely precipitated, as the sulphide, Sb_2S_3, the liquid was heated for some time to drive off the hydrogen sulphide. The precipitate was then collected on a porcelain Gooch filter and washed successively with water, alcohol, ether, and carbon bi-sulphide, the alcohol and ether rendering the precipitate free from water, while the carbon bi-sulphide removed the free sulphur. The crucible with its precipitate was next placed in a hot-air bath which was kept filled with carbon dioxide, while the bath was slowly heated up to about 250° C. and kept at this temperature for one hour.

At the end of that time the bath was cooled down to the normal temperature, but the current of carbon dioxide was continued till the bath was cool.

The crucible and precipitate were weighed and the Sb_2S_3 calculated to metallic antimony.

Determination of Halogens.

The usual gravimetric method was employed for each of the halogens and requires no special comment here.

The atomic weights employed in the calculation of the results are as follows :

Ag	108.0	S	32.0	C	12.0
Cl	35.5	I	127.0	N	14.0
Sb	120.0	Br	80.0	H	1.0

Description of Experiments.

The ground which the following experiments is intended to cover includes a study of compounds formed by the halogen-acid derivatives of aniline and the toluidines with the corresponding halides of antimony.

The method of preparing the salts was to bring the halide of the base together with the corresponding halide of antimony, each constituent being previously dissolved in the corresponding halogen acid.

The results were found to be most satisfactory when each solution was heated before mixing; the base was then added to the metallic chloride.

The plan adopted in making the mixtures was to add the halide of the metal in gradually increasing molecular proportions to one molecule of the halide of the base.

Since in no case the analyses of any of the mixtures indicated that more than one molecule of the halide of the metal had combined with one molecule of the halide of the base, mixtures were not made containing more than three molecules of the halide of the metal to one molecule of the halide of the base.

Similar trials were then made in the other direction, *i. e.*, one molecule of the metallic halide was mixed with a gradually increasing number of molecules of the halide of the organic base in the ratios of 1 to 2, 1 to 3, 1 to 4, and 1 to 6, respectively. The limit of double salt formation in this direction was considered reached, since in many cases the halide of the base crystallized out even in mixtures of 1 to 3, and in no case was a salt found which contained more than four molecules of the halide of the base to one of the antimony.

Every mixture made produced a double salt of some kind. When the solutions were of a proper consistency the formation of the crystals was of a uniform character, and they were easily obtained, as a rule, in that condition. The compounds formed differed markedly in their powers of crystalli-

zation, but as the formation of crystals with well-defined angles and faces would require days and often weeks, no special attempt was made to gather and study the substances crystallographically. Such investigation was further interfered with by the fact that many of the substances rapidly underwent changes which rendered them unfit for that kind of study.

A few notes, however, of a crystallographic character, kindly furnished by Mr. A. C. Spencer, of the Geological Department of this University, will give an idea of the nature of some of the substances in this respect.

As a rule, if the first crops of crystals were found to be uniform in appearance, they were subjected to chemical analysis, the determination of the halogen and the antimony being considered sufficient for the identification of the substance.

The results of the analyses of the compound formed from each mixture are placed in a table at the end of the description of these compounds.

Under each mixture is placed the results of the analysis of the compound obtained from that mixture, and in the smaller table is found the summary of the results of the analyses grouped under the formulas of those compounds which the analyses seem to indicate have been formed.

Experiments with Aniline Hydrochloride and Antimony Trichloride.

The account of the experiments with aniline hydrochloride and antimony trichloride will now be taken up in detail.

From mixture No. 1 (one part of the base to one of the metallic chloride), there crystallized out a colorless salt in thick irregular prisms, which on analysis gave results for chlorine and antimony, as recorded in column 1 of Table I.

On comparing these results with the theoretical values which ought to be obtained if a compound called for by the one at the head of column 1 had been formed, no agreement between these values was found, but as these experimental results did compare with the theoretical per cents of the compound heading column V, it was concluded that a compound was formed, having a composition expressed by the

formula $(C_6H_5.NH_2.HCl)_3.SbCl_3.H_2O$, and which may be called *trianiline chlorantimonite.*

Properties of the Compound.

This substance crystallizes in thick, colorless monoclinic prisms, having the appearance shown in Fig. 1.

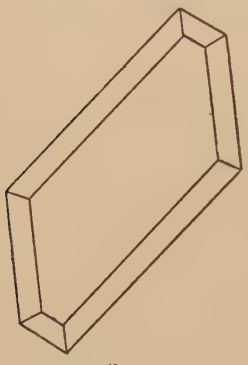

Fig. 1.

The action of a number of solvents was tried, and it was found to dissolve quite readily even in all the dilute mineral acids, as well as in a number of the organic acids in concentrated form, *e. g.*, tartaric and acetic acids. It required rather strong ethyl and methyl alcohol to effect solution.

Water or dilute alcohol precipitated a white antimonyl compound.

On boiling a solution of the salt the odor of nitrophenol was given off.

On gently heating the dry substance in an open tube it was rapidly decomposed, hydrochloric acid being given off.

After exposure to the air for several days the substance acquired an opaque greenish appearance. On keeping specimens for several months no further change in appearance seemed to occur.

The results of an analysis of mixture No. 2, in which the constituents were combined in the proportion of one molecule of aniline hydrochloride to two molecules of antimony trichloride, pointed to a compound of the formula $C_6H_5.NH_2.HCl.SbCl_3.H_2O$.

Monaniline chlorantimonite crystallized out in long, thin, colorless plates. In general its properties were found to be similar to the first salt described.

Discrepancies in the antimony analyses were probably due to the presence of moisture and sulphur in the Sb_2S_3 precipitate. In the later analyses this difficulty was overcome by

washing the precipitate with alcohol, ether and carbon disulphide.

Analyses of mixture No. 3 showed that monaniline chlorantimonite was again formed.

Mixtures four, five and seven, each in turn, produced one and the same compound, *viz.*, *trianiline chlorantimonite*, the one first described above.

The results recorded include the analyses of both first and second crops, but in no case were the second crops found different from the first.

Table I.—Salts of Aniline Hydrochloride and Antimony Trichloride.

	I.		II.		III.		IV.		V.		VI.
	$C_6H_5.NH_2.HCl.SbCl_3$.	$C_6H_5.NH_2.HCl.SbCl_3.H_2O$.	$C_6H_5.NH_2.HCl.(SbCl_3)_2$.	$C_6H_5.HN_2.HCl.(SbCl_3)_3.H_2O$.	$C_6H_5.NH_2.HCl(SbCl_3)_2$.	$C_6C_5.NH_2.HCl(SbCl_3)_2.H_2O$.	$(C_6H_5.NH_2.HCl)_2SbCl_3$.	$(C_6H_5.NH_2.HCl)_2SbCl_3.H_2O$.	$(C_6H_5.NH_2.HCl)_3.SbCl_3$.	$(C_6H_5.NH_2.HCl)_3SbCl_3.H_2O$.	$(C_6H_5.NH_2.HCl)_6.SbCl_3$.
Theor.											
Sb	33.70	32.08	41.20	39.96	44.49	43.53	24.70	23.83	19.51	18.95	18.88
Cl	39.88	37.97	42.66	41.38	43.88	42.92	36.56	35.25	34.63	33.65	33.33
Exp.											
Sb	19.18				32.71		19.01			19.05	
Cl		33.31			37.54					33.54	
Sb	19.93	19.74	34.11	34.65	32.62	32.66	19.50	19.28		19.18	
Cl		33.69	37.36	37.47	38.08	38.13	33.63	33.77		33.50	
Sb			33.90							19.10	
Cl			37.46							33.24	
Sb										19.08	
Cl										33.29	

Summary of Aniline Hydrochloride and Antimony Trichloride Salts.

	I. $[C_6H_5.NH_2.HCl.SbCl_3.H_2O]$.		V. $[(C_6H_5NH_2HCl)_3SbCl_3.H_2O]$.	
	Sb	Cl	Sb	Cl
Theor.	32.08	37.97	18.95	33.65
Exp.	32.71	38.08	19.05	33.54
	32.62	38.13	19.18	33.50
	32.66	37.54	19.10	33.24
	33.51	37.36	19.08	33.29
	33.90	37.47	19.01	33.63
		37.38	19.50	33.77
		37.46	19.28	33.31
			19.18	33.23
			19.74	33.69
			19.93	33.33
			18.88	

Experiments with o-Toluidine Hydrochloride and Antimony Trichloride.

Experiments were next undertaken in the *o*-toluidine series, the line of work being carried out in a manner similar to that followed in the experiments with aniline.

The analyses of the compounds resulting from the several mixtures in this series point to the existence of only one compound, *viz.*, *di-o-toluidine chlorantimonite*, having the composition expressed by the formula $(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3$.

A large quantity of colorless crystals separated out from mixture No. 5, which, when dissolved and treated with hydrogen sulphide, gave no antimony reaction.

The substance was the halide of the base. On pouring off the mother liquor from these crystals, a compound of a different form at once separated out, which proved to be the double salt above mentioned. This substance, as usually formed, did not differ much in appearance from the aniline salts already described.

When allowed to form rapidly the tendency of both the aniline and all the toluidine chlor-antimony salts is to crystallize out in beautiful sheaf-like masses with a satin lustre.

The analytical results of the study of this series are placed in Table II:

Table II.—Salts of o-Toluidine Hydrochloride and Antimony Trichloride.

	I.		II.		III.		IV.		V.		VI.
	$C_6H_4.CH_3.NH_2.HCl.SbCl_3$.	$C_6H_4.CH_3.NH_2,HCl.SbCl_3.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O$.	$(C_6H_4.CH_3.NH_2HCl)_3SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3.H_2O$	$(C_6H_4.CH_3.NH_2.HCl)_6.SbCl_3$.
Theor.											
Sb	32.43		40.23				23.36	22.57	18.26		
Cl	38.38						34.56	33.39	32.42		
Exp.											
Sb	23.96		25.03		25.60		23.65		24.06		
Cl	34.48		34.83		34.97		34.24		34.40		25.6
Sb	23.92		24.99		25.23		23.73		24.14		
Cl	34.52		34.84		34.85		34.41		34.87		

Summary of o-Toluidine and Antimony Trichloride Salts.

IV.

$(C_6H_4.CH_3NH_2.HCl)_2SbCl_3$.

	Sb	Cl
Theor.	23.36	34.56
Exp.	23.65	34.24
	23.73	34.41
	23.96	34.48
	23.92	34.52
		34.40
		34.87
		34.83
		34.84
		34.97
		34.85

Experiments with m-Toluidine Hydrochloride and Antimony Trichloride.

As in the case of *o*-toluidine experiments, the hydrochloride of the *m*-base was mixed in various proportions with the chloride of antimony. On an examination of the compounds obtained from each of the seven mixtures made, only two substances were found which proved to be different from each other. Each of the seven mixtures, except the third, gave a compound having the formula $(C_6H_4.CH_3.NH_2HCl)_3.SbCl_3$, which should be named *tri-m-toluidine chlorantimonite.*

This substance always crystallized in thin orthorhombic tablets in the form of radiating groups, and perfectly transparent and colorless.

Following is a brief crystallographic account of one of the crystals examined :

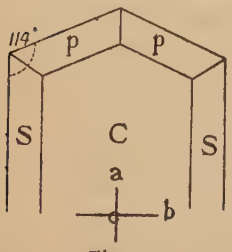

Fig. 2.

Orthorhombic.

C = basal plane.
p = bracypinacoids.
S = macrodomes.
C = ℭ.

Mixture No. 3 gave a compound which on analysis pointed to a substance whose composition should be expressed by the formula $(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3.H_2O$, *di-m-toluidine chlorantimonite.*

An analysis of one sample of the substance pointed to the previous substance without water of crystallization. The only form in which this compound was obtained was in fine granular crystals.

The results of experiments with *m*-toluidine compounds are recorded in Table III.

Table III.—Salts of m-Toluidine Hydrochloride and Antimony Trichloride.

	I.	II.		III.			IV.		V.		VI.	VII.
	$C_6H_4.CH_3.NH_2.HCl.SbCl_3$.	$C_6H_4.CH_3.NH_2.HCl.SbCl_3.H_2O$.	$C_6H_4.CH_3.NH_2.HCl(SbCl_3)_3$.	$C_6H_4.CH_3.NH_2HCl(SbCl_3)_3.H_2O$.	$C_6H_4.CH_3.NH_2.HCl.(SbCl_3)_3$.	$C_6H_4.CH_3.NH_2.HCl.(SbCl_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_4SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_6SbCl_3$.
Theor.												
Sb	32.43	40.23					23.36	22.57	18.26			
Cl	38.38						34.56	33.39	32.42			
Exp.												
Sb	19.87	18.69		20.65	23.11	22.56		18.76	18.82		18.65	17.97
Cl	32.51	32.58		33.19	34.08	33.14		32.35	32.25		32.65	31.97
Sb	19.73	18.66		20.71		22.51		18.78	18.79		18.61	
Cl	32.41	32.43		33.28		33.43		32.19	32.69		32.29	

Summary of m-Toluidine Hydrochloride and Antimony Trichloride Salts.

	V. $[(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.]$		VI. $[(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.H_2O.]$	
	Sb	Cl	Sb	Cl
Theor.	18.61	32.42	22.57	33.39
Exp.	18.61	32.29	22.56	33.14
	18.65	32.35	22.51	33.43
	18.82	32.25	23.11	34.08
	18.79	32.69		33.19
	18.76	32.35		33.28
	18.78	32.19		
	18.69	32.41		
	18.66	32.58		
	17.97	32.43		
	19.03	32.51		
		31.97		
		32.31		

Experiments with p-Toluidine Hydrochloride and Antimony Trichloride.

On carrying out the same general method of experiment with this series of compounds, the analyses of the substances formed from the various mixtures pointed to the formation of only two different bodies, *viz.*, *di-p-toluidine chlorantimonite*, $(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.\frac{1}{2}H_2O$, and *tri-p-toluidine chlorantimonite*, $(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.H_2O$.

Mixtures one, two, three and four produced the second of the above compounds, while the first was formed only by mixture five. The tri-compound forms in colorless granular crystals, while the di-compound is formed in long colorless silky needles. Neither of these compounds seem to undergo any change on being kept for months.

The analytical results are recorded in the following table and summary :

Table IV.—Salts of p-Toluidine Hydrochloride and Antimony Trichloride.

	I.		II.		III.		IV.		V.	
	$C_6H_4.CH_3.NH_2.HCl.SbCl_3$.	$C_6H_4CH_3.NH_2.HCl.SbCl_3.H_2O$.	$C_6H_4.CH_3.NH_2.HCl.(SbCl_3)_2$.	$C_6H_4.CH_3.NH_2.HCl.(SbCl_3)_2.H_2O$.	$C_6H_4.CH_3NH_2.HCl.(SbCl_3)_3$.	$C_6H_4.CH_3NH_2.HCl.(SbCl_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_2.SbCl_3.\frac{1}{2}H_2O$.	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3$.	$(C_6H_4.CH_3.NH_2.HCl)_3.SbCl_3.H_2O$.
Theor.										
Sb	32.43		40.23				23.36	22.97	18.26	17.77
Cl	38.38						34.56	33.95	32.42	31.55
Exp.										
Sb	23.68		23.40		23.68			22.09	18.27	
Cl	33.52		33.66		33.16			33.13	31.54	
Sb	23.58		23.50		24.03			22.61	18.21	
Cl	33.49		33.38		33.08			33.10	28.14	
Sb									18.27	
Cl	33.10								31.46	
Sb									18.11	
Cl									31.55	

Summary of p-Toluidine Hydrochloride and Antimony Trichloride Salts.

	IV. $(C_6H_4.CH_3NH_2HCl)_2.SbCl_3.\frac{1}{2}H_2O$.		V. $(C_6H_4.CH_3NH_2.HCl)_3.SbCl.H_2O$.	
	Sb	Cl	Sb	Cl
Theor.	22.97	33.95	17.77	31.55
Exp.	23.68	33.52	18.27	31.54
	23.58	33.49	18.21	
	23.40	33.66	18.27	31.55
	23.50	33.38	18.11	31.46
	23.68			
	24.03			

Experiments with Aniline Hydrobromide aud Antimony Tribromide.

The following series of mixtures of the above substances were made in hydrobromic acid solution 1 to 1, 1 to 2, 1 to 3, 2 to 1, 3 to 1, 4 to 1, and 6 to 1.

In beaker one there was found a copious crop of fine light-yellow needles. In No. 2 there was a scant crop of two kinds of crystals, one kind being thin, flat, rectangular plates; the other yellow granular crystals. Mixture 3 gave yellow needles, similar in appearance to those in No. 1. In beaker 4 was formed a small crop of yellow needles along with larger yellow granular crystals. A copious crop of light yellow scaly crystals were found in beaker 5. In No. 6 appeared a copious crop of yellow granular crystals. A copious crop of irregular, flat, thick, whitish-yellow plates formed in beaker 7.

As in each case the crystals had formed too quickly to be well defined and uniform, all the crops were redissolved, the olutions somewhat diluted, and again set aside to crystallize out. The next series of crystals were generally of better form. Salts from beakers 1, 2, 3, 4, and 5 crystallized out in centimeter-long, canary-yellow, lath-shaped crystals of the orthorhombic system and of the form shown in the accompanying figure.

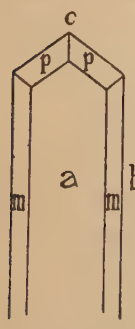

Fig. 3.

The cleavage is parallel to *a*. The crystals also showed parallel extinction in polarized light.

A chemical analysis of each of these five crops resulted in pointing to only one chemical compound, which is represented by the formula $(C_6H_5.NH_2.HBr)_2SbBr_3$, and receives the name *di-aniline-brom-antimonite*.

It is of a canary-yellow color and translucent, stable in the air, undergoing no perceptible change on being kept for several months. The analyses showing its composition are given in the following table.

Mixtures 6 and 7 produced substances which, though of the same yellow color, differed markedly in their crystal habit.

This will be best indicated by the figure, cleavage is parallel to *a* and perfect. Habit tabular and perpendicular to *a*. Orthorhombic system.

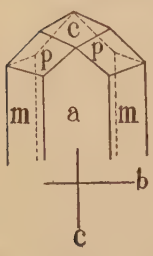

Fig. 4.

a = brachypinacoid.
c = basal plane.
p = macropinacoids.
m = macroprisms.

An analysis of this salt showed it to have an unusual composition, there being four molecules of the halide of the base combined with one molecule of the halide of antimony.

Its composition is expressed by the formula $(C_6H_5.NH_2.HBr)_4SbBr_3.H_2O$, and the compound receives the name *tetraniline bromantimonite*.

It was found impossible to determine the water of crystallization by exposure of the substance over sulphuric acid, as after a short treatment of this kind, dense fumes of hydrobromic acid were given off on opening the desiccator.

On preserving crystals of the substance for some time they gradually became opaque.

The results of the above experiments are recorded in Table V.

Table V.—Salts of Aniline Hydrobromide and Antimony Tribromide.

	I.	II.		III.	IV.		V.	VI.		VII.	
	$C_6H_5.NH_2.HBr.SbBr_3$.	$C_6H_5.NH_2.HBr.SbBr_3.H_2O$.	$C_6H_5.NH_2.HBr.(SbBr_3)_2$.	$C_6H_5.NH_2.HBr(SbBr_3)_2.H_2O$.	$C_6H_5.NH_2.HBr(SbBr_3)_3$.	$C_6H_6.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_5.NH_2.HBr)_2SbBr_3$.	$(C_6H_6.NH_2.HBr)_2SbBr_3.H_2O$.	$(C_6H_5.NH_2.HBr)_3SbBr_3$.	$(C_6H_6.NH_2.HBr)_3SbBr_3.H_2O$.	$(C_6H_5.NH_2.HBr)_4SbBr_3$.	$(C_6H_6.NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_6.NH_2.HBr)_6.SbBr_3$.	$(C_6H_5.NH_2.HBr)_6SbBr_3.H_2O$.
Theor.														
Sb	22.47	26.85		28.71	16.95	16.53	13.60	11.36		11.17	8.55			
Br	59.93	62.64		63 79	56.49	55.10	54.42	53.03		52.14	51.28			
Exp.														
Sb	16.74	17.45		16.53	16.77		16.40			11.26	11.06			
Br	56.75	57.05		56.02	56.56		56.39			52.26	52.16			
Sb		11.59		16.34							11.24			
Br		54.80		58.82							51.97			
Sb											11.07			
Br											52.22			

Summary of Aniline Hydrobromide and Antimony Tribromide Salts.

	IV. $(C_6H_5.NH_2.HBr)_2SbBr_3$		VI. $(C_6H_5.NH_2.HBr)_4SbBr_3.H_2O$.	
	Sb	Br	Sb	Br
Theor.	16.95	56.49	11.17	52.14
Exp.	16.74	56.75	11.06	52.16
	16.45	57.05	11.24	51.97
	16.53	56.02	11.07	52.12
	16.34	55.82	11.26	52.26
	16.77	56.56		
	16.40	56.39		

Experiments with o-Toluidine Hydrobromide and Antimony Tribromide.

The experiments were carried out in the usual manner with this series of substances.

Out of the seven various mixtures which were made, from the appearance of the crystals which were formed, only one kind of compound seemed to be produced.

The crystals of this substance had the same general appearance in each beaker, being of a light yellow color.

The crystallizing force of the substance seemed to be weaker than that of any of the compounds previously analyzed.

Small, short, blunt prisms crystallized out, both as first and second crops, from the same mixture.

Determinations of antimony and bromine led to the conclusion that *tri-o-toluidine bromantimonite*, $(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$, was the only compound which forms from the constituents employed.

A number of analyses are given in the following table :

Table VI.—Salts of o-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4.CH_3.NH_2.HBr.SbBr_3$.	$C_6H_4.CH_3.NH_2.HBr.SbBr_3.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2HBr)_3SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_4.CH_3NH_2HBr)_6SbBr_3$.	$(C_6H_4.CH_3.NH_2HBr)_6SbBr_3.H_2O$.
Theor.														
Sb	21.89	21.20	26.43	25.92	28.39	27.99	16.30	15.91	12.98	12.74	10.80	10.62	8.06	7.97
Br	58.39		61.56		63.09		54.35	53.05	51.95	50.95	50.36	49.56		
Exp.														
Sb			13.37		12.80		12.67		12.87		12.78		12.86	
Br	50.63		51.70		50.62		50.76		51.71		51.26		51.41	
Sb														
Br	50.57				51.84		51.57						51.51	
Sb	13.17													
Br	51.07													

Summary of o-Toluidine Hydrobromide and Antimony Tribromide Salts.

	V. $(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.	
	Sb	Br
Theor.	12.98	51.95
Exp.	13.17	51.70
	13.37	51.84
	12.80	51.07
	12.67	51.57
	12.87	51.70
	12.78	51.26
	12.86	51.51
		51.41

Experiments with m-Toluidine Hydrobromide and Antimony Tribromide.

Experiments were made in this series with various mixtures of the two constituents. Out of the seven combinations made only one kind of compound was found on analysis. This substance crystallized out in each beaker in long, very pale-yellow, silky needles. The air-dried salt was more opaque and yellower than when seen in the mother-liquor. An analysis of the result of each mixture pointed to one compound only, and this should have the composition expressed by the formula $(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$, and called *di-m-toluidine brom-antimonite.*

Table VII.—Salts of m-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.	III.		IV.		V.	VI.		VII.
	$C_6H_4.CH_3.NH_2.HBr.SbBr_3$.	$C_6H_4.CH_3.NH_2.HBr.SbBr_3.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_2Sb_2Br_3H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_3.SbBr_3.H_2O$	$(C_6H_4.CH_3.NH_2.HBr)_4.SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3.H_2O$	$(C_6H_4.CH_3NH_2HBr)_6SbBr_3$
Theor.													
Sb	21.89	21.20	26.43	28.39		16.30		12.98	10.80			8.06	
Br	58.39	56.53	61.56	63.09		54.35		51.95	50.36				
Exp.													
Sb	15.89			15.65		16.66			16.45			15.96	
Br	54.27		54.49	54.27		54.38		54.03	54.93			54.20	
Sb						16.31							
Br			54.86			54.49		53.93				54.25	

Summary of m-Toluidine Hydrobromide and Antimony Tribromide Salts.

	IV. $(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	
	Sb	Br
Theor.	16.30	54.35
Exp.	16.31	54.49
	16.66	54.86
	16.45	54.38
	15.96	54.03
	15.89	53.93
	15.65	54.49
		54.20
		54.25
		54.27
		54.27
		54.93

Experiments with p-Toluidine Hydrobromide and Antimony Tribromide.

The mixtures of the constituents were made in the usual way in hydrobromic acid solution. Mixtures 1, 2, 4, 5, and 7 all gave crops of silver white needles.

Repeated attempts were made to get a salt from mixture No. 6, but it was possible only to obtain the *p*-toluidine hydrobromide from the solution.

Mixture No. 3 gave a crop of very small lemon-yellow plates.

Owing to the ease with which the white salts give up or take up water of crystallization it was difficult to get sharp analytical data. The analyses of all the salts obtained seem to point to the existence of three different compounds, and one of them also with water of crystallization. They were as follows: *Di-p-toluidine bromantimonite*, $(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_3$, the same compound with one molecule of water of crystallization, $(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_3.H_2O$, *tri-p-toluidine bromantimonite*, $(C_6H_4.CH_3.NH_2.HBr)_3.SbBr_3$, and *tetra-p-toluidine bromantimonite* $(C_6H_4.CH_3.NH_2.HBr)_4.SbBr_3$. In dry air these compounds are canary yellow; but if exposed to the air on a damp day they change over to snow-white. The compound which crystallized out from mixture 3, in the form of small plates, seems to be quite stable as to its color—it remains yellow constantly.

The substance which crystallized from mixture 1, although when analyzed pointed to the same compound *without* water of crystallization, crystallized in needles, so that the taking up of water by the one substance and not by the other may depend upon crystalline form.

The yellow color can be restored in all three compounds by gently heating a portion on a piece of platinum foil.

The analyses of the compounds are tabulated in the usual manner in Table VIII.

Table VIII.—Salts of p-Toluidine Hydrobromide and Antimony Tribromide.

	I.		II.		III.		IV.		V.		VI.		VII.	
	$C_6H_4CH_3.NH_2.HBr.SbBr_3$.	$C_6H_4.CH_3.NH_2.HrB.SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)(SbBr_3)_2$.	$(C_6H_4.CH_3.NH_2.HBr)(SbBr_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2$.	$C_6H_4.CH_3.NH_2.HBr(SbBr_3)_2.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_2SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_4SbBr_3$.	$(C_6H_4.CH_3NH_2.HBr)_4SbBr_3.H_2O$.	$(C_6H_4.CH_3.NH_2.HBr)_6SbBr_3$.	$(C_6H_4.CH_3.NH_2.HBr)_6SbBr_3.H_2O$.
Theor.														
Sb	21.89	21.20	26.43	25.92	28.39	27.99	16.30	15.91	12.98	12.74	10.80	10.62	8.06	7.97
Br	58.39		61.56		63.09		54.35	53.05	51.95	50.95	50.36	49.56		
Exp.														
Sb			16.04						12.59				15.09	
Br			52.73		54.78				51.45				52.90	
Sb			15.73				10.85							
Br	53.55				54.72				51.49				52.58	
Sb							10.65							
Br	53.94				54.54		49.83							
Sb														
Br	54.15						50.00							
Sb														
Br	53.70													

Summary of p-Toluidine Hydrobromide and Antimony Tribromide Salts.

	IV.		V.		VI.	
	Sb	Br	Sb	Br	Sb	Br
Theor.						
	16.30	54.35	15.91	53.05	12.98	51.95	10.80	50.36
Exp.						
		53.94	16.04	52.73	12.59	51.45	10.85	50.00
		53.55	15.73	52.52		51.49	10.65	49.83
		54.15		52.48				
		53.70		52.90				
		54.78		52.58				
		54.72						
		54.54						

On exposing the compound (which on analysis showed the presence of water of crystallization) in the desiccator over concentrated sulphuric acid, there was a constant loss of weight, due to the evolution of hydrobromic acid, presumably.

Experiments with Aniline Hydriodide and Antimony Triiodide.

Study in this series was begun with the aniline salt. Some difficulty was experienced here, since it was necessary to prepare hydriodic acid only in such quantities as would be immediately needed, owing to its rapid decomposition. It was also difficult to avoid the separation of free iodine when heating the mixtures.

A convenient method for making hydriodic acid is to gradually add 4 grams dry yellow phosphorus, in small pieces, to 44 grams crystallized iodine in a round-bottomed, hard-glass flask. When all the phosphorus has been added and the reaction-product, phosphorus triiodide, is quite cool, 6 grams water is added to the solidified mass. The flask is then connected with a second bottle or flask containing about 50 cc. water.

The first flask is very gently heated to drive over the hydriodic acid.

The water absorbs the acid without danger of the former being drawn back into the distilling flask, if the tube is about 1 centimenter above the surface of the water.

The mixtures of the aniline and antimony halides were made up in the usual proportions hitherto employed.

A crop of finely divided granular scarlet crystals separated from mixture No. 1. On drying these seemed to undergo no change. A determination of antimony and iodine clearly pointed to the existence of a compound whose composition should be expressed by the formula $C_6H_5.NH_2.HI.SbI_3$, *monaniline iodantimonite*.

Out of mixture No. 2, small, almost microscopic, scarlet octahedra with modified edges crystallized out. An analysis of these revealed no new compound.

Crystals from mixture 3, again in the form of modified and

twinned octahedra, proved on analysis to be identical with the first compound discovered in this series.

Mixtures 4 and 6 yielded nothing new in the way of double salts. Mixture No. 5, on the other hand, yielded a beautiful crop of fine carmine needles, which on analysis proved to be a combination not yet met with in the present investigation. The compound is composed of 3 molecules of aniline hydriodide and two of antimony triiodide, expressed by the formula $(C_6H_5.NH_2HI)_3(SbI_3)_2$, *trianiline di-iodantimonite*.

The last mixture examined was that in which the ratio of the constituents was 6 to 1. A new compound seemed to be formed here. The mixture from which the compound was finally obtained yielded at first only a large crop of the halide of the base. On evaporating the mother-liquor, a crop of uniform golden-yellow plates was obtained. These were dried and tested for antimony. It was found to be present in considerable quantity. As soon as the crystals were drained off they began to undergo change in color from golden-yellow to orange-red. When dry they were analyzed and gave results pointing to the formula $(C_6H_5.NH_2.HI)_4(SbI_3)$, *tetraaniline iodantimonite*.

The analytical results of the study of this series are gathered into Table IX.

Table IX.—Aniline Hydriodide and Antimony Triiodide.

	I.		II.	III.	IV.	V.	Va.	VI.	VII.
	$C_6H_5.NH_2.HI.SbI_3$.		$C_6H_5.NH_2.HI.(SbI_3)_2$.	$C_6H_5.NH_2.HI.(SbI_3)_3$.	$(C_6H_5.HN_2.HI)_2SbI_3$.	$(C_6H_5.NH_2.HI)_3SbI_3$.	$(C_6C_6.NH_2.HI)_3(SbI_3)_2$	$(C_6H_5.NH_2.HI)_4SbI_3$.	$(C_6H_5.NH_2HI)_6SbI_3$.
Theor.									
Sb	16.62	16.21	19.62			10.31	14.41	8.66	
I	70.36	68.64	72.69	73.08	67.34	65.46	68.64	64.19	62.56
Exp.									
Sb	16.78					14.52			8.71
I	70.15		70.30	70.14	70.84	68.23		70.29	64.32
Sb	16.80					14.48			8.24
I	70.44		70.39	70.10	70.08	68.31		69.99	64.31
Sb						14.14			
I						68.35			64.47
Sb						14.34			
I						68.75			

Summary of Aniline Hydriodide and Antimony Triiodide Salts.

I.		Va.		VI.	
Sb	I	Sb	I	Sb	I
Theor.					
16.62	70.36	14.41	68.64	8.66	64.19
Exp.					
16.78	70.15	14.52	68.23	8.71	64.32
16.80	70.44	14.48	68.31	8.24	64.31
	70.31	14.14	68.35		64.47
	70.39	14.34	68.75		
	70.14				
	70.10				
	70.84				
	70.08				
	69.99				
	70.29				

Experiments with o-Toluidine Hydriodide and Antimony Triiodide.

The usual experiments were made with the above ingredients and no difficulty was experienced in obtaining well-characterized products in the case of each experiment. The double salts which crystallized out from each of the first 3 mixtures had the same general appearance, consisting of short blunt needles of a brick-red color. Analyses of the 3 sets of crystals pointed to one and the same compound, containing one molecule of each of the original ingredients. The formula expressing the composition may be shown by the following: $C_6H_4.CH_3NH_2.HI.SbI_3$, *mon-o-toluidine iodantimonite*.

An examination of the double salts formed from mixtures 4, 5, 6, and 7 indicated that a new variety had been formed. The appearance of the crystals in the above cases was quite different from that of the first compound described. They consisted of irregular-shaped bronze-colored leaves. Analyses of a sample of each set indicated that only one individual had been formed, *viz.*, *tri-o-toluidine diiodantimonite* $(C_6H_4.CH_3.NH_2.HI)_3.(SbI_3)_2$.

Table X.—Salts of o-Toluidine Hydriodide and Antimony Triiodide.

	I.	II.		III.	IV.	V.	Va.	VI.	VII.
	$C_6H_4.CH_3.NH_2.HI.SbI_3$.	$C_6H_4.CH_3.NH_2.HI(SbI_3)_2$.	$C_6H_4.CH_3.NH_2.HI(SbI_3)_2.H_2O$.	$C_6H_4.CH_3.NH_2.HI(SbI_3)_3$.	$(C_6H_4.CH_3.NH_2.HI)_2SbI_3$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3$.	$(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$.	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3$.	$(C_6H_4.CH_3.NH_2.HI)_6SbI_3$.
Theor.									
Sb	16.30	19.40			12.35	9.95	14.06	8.32	6.28
I	69.02	71.06	70.83		65.40	63.18	66.96	61.69	59.81
Exp.									
Sb	16.19				13.89				
I	68.44	68.63		68.89	66.71	66.67		66.33	66.43
Sb	15.88								
I	68.36	68.70		69.00	66.78	66.37			66.25

Summary of o-Toluidine Hydriodide and Antimony Triiodide Salts.

	I. $C_6H_4CH_3NH_2.HI.SbI_3$.		Va. $(C_6H_4CH_3NH_2.HI)_3(SbI_3)_2$.	
	Sb	I	Sb	I
Theor.	16.30	69.02	14.06	66.99
Exp.	16.19	68.44	13.89	66.71
	15.88	68.36		66.78
		68.63		66.33
		68.70		66.43
		68.89		66.25
		69.00		66.37
				66.67

Experiments with m-Toluidine Hydriodide aud Antimony Triiodide.

Mixtures of the above ingredients were made up in the usual way and well-defined crystals began to appear in each beaker as soon as the solutions were cool. On examination of the various sets of crystals, by means of the lens, they appeared to be all of the same general character. After removal from the solutions, and drying, the crystals were in the form of glistening brick-red prisms.

Chemical analysis pointed, in the case of each of the deposits, to the formation of only one chemical compound. This proved to be *tri-m-toluidine diiodantimonite*, having the formula, $(C_6H_4.CH_3.NH_2.HI)_3.(SbI_3)_2$.

This substance, like the corresponding ortho-compound, seems to possess a strong crystallizing force. A statement of the analytical results leading to the above formula will be found in the following tables:

Table XI.—Salts of m-Toluidine Hydriiodide, and Antimony Triiodide.

	I.	II.	III.	IV.	V.	Va.	VI.	VII.
	$C_6H_4.CH_3.NH_2.HI.SbI_3$.	$C_6H_4.CH_3.NH_2.HI.(SbI_3)_2$	$C_6H_4.CH_3.NH_2.HI.(SbI_3)_3$.	$(C_6H_4.CH_3.NH_2.HI)_2SbI_3$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3$.	$(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3$.	$(C_6H_4.CH_3.NH_2.HI)_6SbI_3$.
Theor.								
Sb					14.06			
I					66.96			
Exp.								
Sb				13.74				
I	66.67	66.93	66.86	66.53	66.95	66.89		66.68
Sb								
I	67.00	66.78	67.08	67.03	66.74	66.26		66.76

Summary of m-Toluidine Hydriodide and Antimony Triiodide Salts.

	Va. $(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$.	
	Sb	I
Theor.	14.06	66.96
Exp.	13.74	66.77
		67.00
		66.93
		66.78
		66.86
		67.08
		66.53
		67.03
		66.95
		66.74
		66.89
		66.26
		66.68
		66.76

Experiments with p-Toluidine Hydriodide and Antimony Triiodide.

In working with this series some difficulty was met with in obtaining well-characterized and uniform crystals in the same beaker. From nearly every mixture worked with there crystallized out side by side light orange-colored blunt prismatic crystals and darker orange-colored needles. The prismatic forms seemed to be the more soluble of the two, and by regulating the concentration of the solution it was possible to obtain a uniform crop of the needle variety. Specimens of the light prismatic type were gotten out, but on being transformed to a porous earthenware plate, began to turn orange-red in a very short time.

Analyses of both kinds of crystals, after being dried in the air, showed that there was no difference in their composition. The composition and name of this compound are respectively, $C_6H_4.CH_3.NH_2.HI.SbI_3$ and *mono-p-toluidine iodantimonite.*

Table XII.—Salts of p-Toluidine Hydriodide and Antimony Triiodide.

	I.		II.		III.		IV.		V.	VI.	VII.	
	$C_6H_4CH_3.NH_2.HI.SbI_3.$	$C_6H_4.CH_3.NH_2.HI.SbI_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)(SbI_3)_2.$	$(C_6H_4.CH_3.NH_2.HI)(SbI_3)_2.H_2O.$	$C_6H_4.CH_3.NH_2.HI(SbI_3)_3.$	$C_6H_4.CH_3.NH_2.HI(SbI_3)_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_3SbI_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_4SbI_3.H_2O.$	$(C_6H_4.CH_3.NH_2.HI)_6SbI_3.$	$(C_6H_4.CH_3.NH_2.HI)_6SbI_3.H_2O.$
Theor.												
Sb	16.30		19.40	19.12			12.35		9.95	8.32	6.28	
I	69.02	67.37	71.06	70.83			65.40		63.18	61.69	59.81	
Exp.												
Sb			16.58		16.88		16.08					
I	69.12		68.86						68.51	68.56	68.42	
Sb			16.27				16.75					
I	69.30		68.67						68.43		68.37	
Sb							16.34					

Summary of p-Toluidine Hydriodide and Antimony Triiodide Salts.

I.

$C_6H_4.CH_3.NH_2.HI.SbI_3.$

	Sb.	I.
Theor.	16.30	69.02
Exp.	16.58	69.12
	16.27	69.30
	16.88	68.86
	16.08	68.67
	16.75	68.51
	16.34	68.43
		68.56
		68.42
		68.37

LIST OF SUBSTANCES DESCRIBED.

Chlorides.

Salts of Aniline Hydrochloride and Antimony Trichloride.

$C_6H_5.NH_2.HCl.SbCl_3.H_2O$. *Monaniline chlorantimonite.*

$(C_6H_5.NH_2.HCl.)_3SbCl_3.H_2O$. *Trianiline chlorantimonite.*

Salts of *o*-Toluidine Hydrochloride and Antimony Trichloride.

$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3$. *Di-o-toluidine chlorantimonite.*

Salts of *m*-Toluidine Hydrochloride and Antimony Trichloride.

$(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3$. *Tri-m-toluidine chlorantimonite.*

$(C_6H_4.CH_3.NH_2HCl)_2SbCl_3.H_2O$. *Di-m-toluidine chlorantimonite.*

Salts of *p*-Toluidine Hydrochloride and Antimony Trichloride.

$(C_6H_4.CH_3.NH_2.HCl)_2SbCl_3.\frac{1}{2}H_2O$. *Di-p-toluidine chlorantimonite.*

$(C_6H_4.CH_3.NH_2.HCl)_3SbCl_3.H_2O$. *Tri-p-toluidine chlorantimonite.*

Bromides.

Salts of Aniline Hydrobromide and Antimony Tribromide.

$(C_6H_5.NH_2.HBr)_2SbBr_3$. *Dianiline bromantimonite.*

$(C_6H_5.NH_2HBr)_4SbBr_3.H_2O$. *Tetraniline bromantimonite.*

Salts of *o*-Toluidine Hydrobromide and Antimony Tribromide.

$(C_6H_4.CH_3.NH_2.HBr)_3SbBr_3$. *Tri-o-toluidine bromatimonite.*

Salts of *m*-Toluidine Hydrobromide and Antimony Tribromide.

$(C_6H_4.CH_3.NH_2HBr)_2SbBr_3$. *Di-m-toluidine bromantimonite.*

Salts of *p*-Toluidine Hydrobromide and Antimony Tribromide.

$(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_3$. *Di-p-toluidine bromantimonite.*

$(C_6H_4.CH_3.NH_2.HBr)_2.SbBr_3.H_2O$. " " "

$(C_6H_4.CH_3.NH_2.HBr)_3.SbBr_3$. *Tri-p-toluidine bromantimonite.*

$(C_6H_4.CH_3.NH_2.HBr)_4.SbBr_3$. *Tetra-p-toluidine bromantimonite.*

Iodides.

Salts of Aniline Hydriodide and Antimony Triiodide.

$C_6H_5.NH_2.HI.SbI_3$. *Monaniline iodantimonite*

$(C_6H_5.NH_2.HI)_3.(SbI_3)_2$. *Trianiline di-iodantimonite.*

$(C_6H_5.NH_2.HI)_4.SbI_3$. *Tetraniline iodantimonite.*

Salts of *o*-Toluidine Hydriodide and Antimony Triiodide.

$C_6H_4.CH_3.NH_2.HI.SbI_3$. *Mon-o-toluidine iodantimonite.*

$(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$. *Tri-o-toluidine di-iodantimonite.*

Salts of *m*-Toluidine Hydriodide and Antimony Triiodide.

$(C_6H_4.CH_3.NH_2.HI)_3(SbI_3)_2$. *Tri-m-toluidine di-iodantimonite.*

Salts of *p*-Toluidine Hydriodide and Antimony Triiodide.

$C_6H_4.CH_3.NH_2.HI.SbI_3$. *Mono-p-toluidine iodantimonite.*

All of the substances above mentioned are found to come within the scope of the law regarding the composition of the double-halides, proposed by Professor Remsen. The formation of the three substances which do not appear to conform to this law has already been discussed in the introduction.

BIOGRAPHICAL.

Howard Haines Higbee, the author of this dissertation, was born at Lodi, Ohio, on the 13th of August, 1861. His early education was obtained in the schools of Cleveland, Ohio. He entered Yale College in 1880, and graduated with the bachelor's degree, in 1884. Four years were then spent by him as an instructor in general studies in secondary schools.

In 1889 he entered the Johns Hopkins University as a student of chemistry, with which he has since been connected, with the exception of an interval of two years which was spent in chemical work and study in New York and in Munich.